# High electrostrictive strain under high mechanical stress in electron-irradiated poly(vinylidene fluoride-trifluoroethylene) copolymer

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In this letter, we show that the electric field induced strain in the electron irradiated poly(vinylidene fluoride-trifluoroethylene) copolymer can generate high strain even under a high mechanical stress. The observed change in strain with stress is due to the electrostrictive coupling of the local polarization with stress, and can be directly related to the change of the induced strain with temperature. The results indicate that the field induced strain observed in the films investigated is indeed from the local polarization regions in the material, and is electrostrictive in nature. © *1999 American Institute of Physics.* [S0003-6951(99)03743-2]

Polymers which can generate high electric field induced strain are very attractive for a broad range of applications such as artificial muscles, robots, ultrasonic transducers for medical diagnosis, sonar, and active control of mechanical systems.[1] It was found recently that under a proper electron irradiation treatment, a massive electrostrictive strain can be induced in poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] copolymers. Because of the high elastic modulus of the material, it also possesses a high elastic energy density.[2–5] Being a polymeric material, the electromechanical response under high mechanical load is always a concern, that is, whether the material can maintain the strain level when subject to high external stresses. For example, several polymers such as polyurethane, polybutadiene, silicone rubber etc, were observed to generate very high electric field induced strains up to ~10%.[6–9] But due to the fact that these materials have a very low elastic modulus and the strain is caused by the Maxwell stress effect, the elastic energy density of these polymers is low and the strain diminishes even under the mechanical constraints of the metal electrodes deposited on the samples.[6] In this letter, we demonstrate that the irradiated P(VDF-TrFE) copolymer films can generate a high strain under a high external load. In addition, the experimental results also show that due to the ferroelectric nature of the material, the mechanical load effect on the field induced strain can be directly linked to the variation of the strain with temperature.

The PVDF($x$)−TrFE($1-x$) copolymer with $x=65$ mol % was chosen for this study. Among the compositions investigated, this composition showed the highest electrostrictive strain in both the longitudinal and transverse directions (parallel and perpendicular to the applied electric field). The copolymer powder was purchased from Solvay and Cie, Bruxelles, Belgium. The unstretched and uniaxially stretched (4.5×) films of thickness ~20–30 $\mu$m were prepared by melt pressing and solution casting methods, respectively. In order to improve the crystallinity and also to remove residual solvent, the films were annealed in a vacuum oven at 140 °C for 16 h. These films were irradiated in a nitrogen atmosphere with 2.55 MeV electrons at 95 °C and with a 60 Mrad dose.

A cantilever based dilatometer was used to measure the strain along the stretching direction (transverse strain, $S_1$) at different tensile stresses ($\sigma_T$) applied in the same direction.[4] The strain along the thickness direction (longitudinal strain, $S_3$) was measured at different hydrostatic pressures ($\sigma_h$) using a piezoelectric bimorph based sensor.[9] In this setup, one end of the piezoelectric bimorph was fixed while the other was in contact with the sample. Under an ac electric field, the expansion and contraction along the sample thickness direction generate the corresponding bending motion in the bimorph sensor. Through the piezoelectric effect, an electrical output voltage which is perpotional to the bending of bimorph is observed. Both the setups were designed and developed specifically for strain measurements in polymer films under load. In both cases, the ac electric field is applied along the film thickness with frequencies ranging from 1 to 10 Hz.

Since the magnitude of the transverse strain is higher for stretched films in comparison to unstretched films, the 65/35 stretched films were used to measure the transverse strain at different tensile stresses along the stretching direction. As can be seen from Fig. 1, under a constant electric field, the transverse strain initially increases with the load and reaches to a maximum at the tensile stress of about 20 MPa. Upon further increase of the load, the field induced strain is reduced. One important result revealed by the data is that even under a tensile stress of 45 MPa, the strain generated is still nearly the same as that it was without load, indicating that the material has a very high load capability.

The longitudinal strain for unstretched 65/35 mol % films as a function of hydrostatic pressure was measured and the data is presented in Fig. 2. As can be seen, at low driving electric fields, the strain does not change much with pressure. On the other hand, for high fields it shows increases with pressure. Due to the limitation of the experimental setup, we could not apply pressure higher than 8.2 MPa.

The results from both experiments clearly demonstrate that the electrostrictive P(VDF-TrFE) copolymer has a high load capability and maintains its strain level even under a very high mechanical load, which is in contrast to many other polymeric materials.[6–9] However, the increase of the field induced strain with load and the strain maximum observed in Fig. 1 seems to be puzzling. In the following, we

 

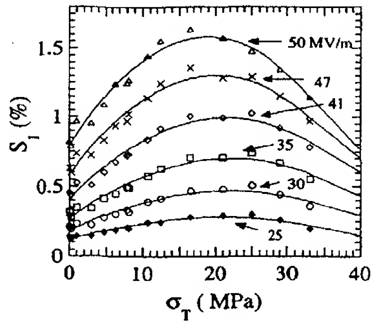


FIG. 1. Effect of tensile stress ($\sigma_T$) on electric field induced transverse strain ($S_1$) measured at room temperature under different driving electric field strengths.

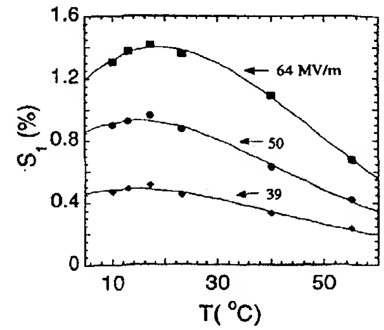


FIG. 3. Variation in electric field induced transverse strain ($S_1$) as a function of temperature measured under stress free conditions at different electric field strengths.

will be showing that the observed phenomena can be understood by considering the electrostrictive coupling of the local polarization with stress in this relaxor ferroelectric material.

It is well known that the unirradiated P(VDF-TrFE) 65/35 mol % copolymer is a normal ferroelectric polymer with a Curie temperature near 70 °C.[10] After the irradiation, we have shown that the material is transformed into a relaxor ferroelectric, which exhibits a large electrostrictive strain.[2] According to the Landau–Devonshire phenomenological theory, when a normal ferroelectric material is subjected to an external stress, its Curie point will shift, which can be described as[11,12]

$$\Delta T = 2\epsilon_0 C Q \Delta\sigma, \tag{1}$$

where $\Delta T$ is the shift of the Curie temperature, $\epsilon_0$ is permitivity in free space, $C$ is Curie–Weiss constant, $\sigma$ is the applied stress, and $Q$ is electrostrictive coefficient. Therefore, depending on the sign of the electrostrictive coefficient and the applied stress, the shift of the Curie point can be either positive (to higher temperature) or negative (to lower temperature). For a relaxor ferroelectric, if we use the simple Smolensky model[13] that a relaxor ferroelectric can be regarded as consisting of local polar regions with different Curie points over a broad temperature range, Eq. (1) can still be used to provide a qualitative understanding of the data.

For the irradiated P(VDF-TrFE) copolymer, it is also shown that the strain is proportional to the square of the induced polarization $P$:[2]

$$S = QP^2. \tag{2}$$

The relevant electrostrictive coefficients used in Eq. (1) for the irradiated copolymer are: $Q_{13}$ (transverse coefficient, related to the transverse tensile stress) and $Q_h$ (volume coefficient, related to the hydrostatic pressure). From early experimental results, it has been shown that $Q_{13}>0$ and $Q_h<0$.[5] Therefore, under a transverse tensile stress, $\Delta\sigma_T>0$, and Eq. (1) dictates that the applied tensile stress will shift the Curie temperature downwards. In an analogy, under hydrostatic pressure, $\Delta\sigma_h<0$, and with increased pressure, the Curie temperature will also move downwards. Combining this with the results in Figs. 1 and 2 suggests that at temperatures near room temperature, both the longitudinal and transverse strains of the samples studied should increase as the temperature is reduced and will reach to a maximum at a temperature below room temperature.

Figures 3 and 4 present the temperature dependence of the transverse strain for the stretched film and the longitudinal strain for the unstretched film measured under stress free conditions at a field range similar to those used in Figs. 1 and 2. Figure 3 shows that for the transverse strain measured in the stretched sample, there is a broad maximum at a temperature near 17 °C in the electric field range measured, which seems to be consistent with the data in Fig. 1. For the longitudinal strain, the temperature limitation of the setup prevents the experiment from being performed below room temperature, and the results in Fig. 4 are consistent with the data in Fig. 2. That is, the field induced strain decreases with

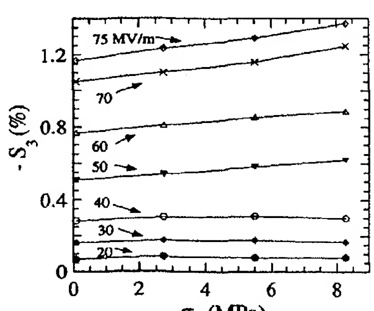


FIG. 2. Effect of hydrostatic pressure ($\sigma_h$) on electric field induced longitudinal strain ($S_3$) measured at room temperature under different driving electric field strengths.

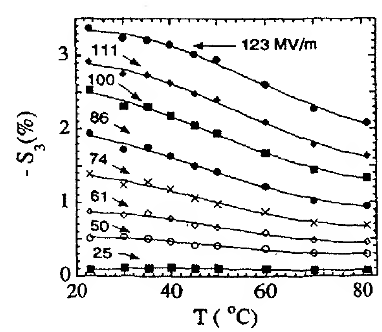


FIG. 4. Variation in electric field induced longitudinal strain ($S_3$) as a function of temperature measured under stress free condition at different electric field strengths.

temperature. It should be pointed out that due to the nature of relaxor ferroelectric material, the induced strain changes with stress or temperature are also dependent on the level of the driving electric field. For the unstretched sample, the data in Fig. 4 seems to indicate that there is a weak strain maximum at a temperature near 35 °C when the measurement was made under a field of 25 MV/m.

From the data presented in Figs. 1 and 3 for the stretched films and in Figs. 2 and 4 for unstretched films, one may obtain the effective electrostrictive coefficients using Eq. (1) if the Curie–Weiss constants are known for the two samples. Using the Curie–Weiss relation, $\epsilon = C/(T-T_c)$, where $\epsilon$ is the permitivity of the material,[12] the values of the Curie–Weiss constants ($C=4002$ and 3475) and Curie–Weiss temperatures ($T_c=10.24$ and 28 °C) were calculated for unirradiated stretched and unstretched films, respectively. These values are found to be close to the values reported by others.[10] The value of $Q_{13}=4.6\,\mathrm{m}^4/\mathrm{C}^2$ is calculated from Eq. (1) using $\Delta T=6\,°\mathrm{C}$ (Fig. 3) and $\Delta\sigma_T=18.4\,\mathrm{MPa}$ (Fig. 1), which is very close to the value of $Q_{13}=4.9\,\mathrm{m}^4/\mathrm{C}^2$ obtained directly from the strain and polarization using Eq. (2).[5] Although for a system as complicated as the irradiated P(VDF-TrFE) copolymer, we do not expect that the analysis presented can be used quantitatively, the consistency in the effective electrostrictive coefficient obtained from the two sets of data does indicate that the observed change of the induced strain with stress is due to the electrostrictive coupling of the local polarization with stress in this material. For unstretched films, by comparing the slopes from the curves under 75 MV/m in Fig. 2 and under 74 MV/m in Fig. 4, we obtain $Q_h=-10.8\,\mathrm{m}^4/\mathrm{C}^2$ which is also consistent with $Q_h=-6\,\mathrm{m}^4/\mathrm{C}^2$ obtained directly from the measured volume strain with polarization.[5] The results obtained here clearly indicate that the field induced strain is due to the local polarization in the material and is electrostrictive in nature. The data presented show that the variation of the field induced strain with stress can be related qualitatively to the change in strain with temperature through Eq. (1) even for a complicated system such as the relaxor ferroelectric P(VDF-TrFE) copolymer. Furthermore, the data show that the electrostrictive strain from the irradiated P(VDF-TrFE) copolymer has a high load capability.

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